



Application of Anion- π Interaction on Supramolecular Self-Assembly

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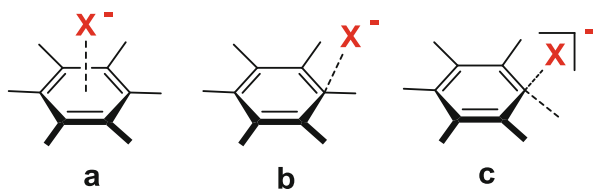
10.1 Introduction

The study of anion- π interactions should be dated to 1993, when Schneider and coworkers described the attractive interaction between negative species and polarizable aryl parts [1]. There are no successive reports after that. Almost 10 years later in 2002, Mascal [2], Deyà [3], and Alkorta [4] at the same time published their independent theoretical studies on energetical favorable interaction between anions and typical electron-deficient aromatics such as triazine, hexafluorobenzene, and perfluoroaromatic compounds. Deyà also termed this interaction as anion- π interaction, reassembling its electrostatic antipode cation- π interaction. A rapid development of anion- π interactions has been witnessed ever since. Various computational studies have been conducted to confirm existence and probe the nature of anion- π interactions. Subsequent experimental efforts, either through incorporating simple

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Fig. 1 Interaction geometries of anion- π interactions



electron-deficient arenes into macrocyclic and supramolecular skeletons [5–9] or employing extended π units such as naphthalenediimides (NDI) [10, 11] and hexaazatriphenylene-hexacarbonitrile (HAT(CN)₆) [12, 13], have exemplified and demonstrated not only the existence but also the marvelous applications of anion- π interactions. Now anion- π interaction has been realized as one of the important driving forces in anion recognition, sensing, ion channel, and catalysis. It is worth addressing that utilizing anion- π interactions as a driving force to direct self-assembly, however, remains largely unexplored. This hindrance is mainly caused by the various interaction modes in anion- π interactions. In sharp contrast to cation- π interaction where cations are exclusively located over the center of an aromatic ring, in anion- π , three types of interaction geometries, i.e., the typical non-covalent anion- π complex (Fig. 1a) and weak and strong σ -type motifs complexes B and C, were suggested being energetically favorable (Fig. 1b, c) [6]. The versatile binding geometries result in reduced directionality and increased difficulty on rational design. Despite the significant challenge in anion- π -directed self-assembly, remarkable achievements though still very few have been witnessed during the past decade. Through cooperating anion- π with other non-covalent interactions and/or rationally designing the organic and anionic building units to maximize the strength and to confine the directionality of anion- π interactions, intriguing self-assembly structures have been obtained. This review will give a summary of anion- π -controlled self-assembly, with efforts mainly focusing on self-assembly structures that anions serve as template, as primary building units, and as secondary building units. The extensive reports on cation coordination systems where anion- π is usually auxiliary and barely affects the assembly entity are beyond the scope of this review.

10.2 Theoretical Study of Anion- π Interactions

It is well known that benzene possesses negative electrostatic potential on the aromatic ring, the interaction between electron-rich aromatics and positively charged species, i.e., cation- π interaction has been widely recognized in supramolecular chemistry and biosystems [14]. Interaction of benzene ring with electron-rich species has ever been regarded to be disfavored thermodynamically. This “old” knowledge was argued by Alkorta’s calculations in 1997 [15], when in their report they suggested the favorable interaction of hexafluorobenzene, an electron-deficient aromatic ring, with several electron-donating small molecules

such as HF, LiH, and HCN. Two years later, Dougherty [16] and Besnard [17] independently reported theoretical studies on interaction of water and hexafluorobenzene, the so-called lone-pair electron- π interaction. The binding energy was predicted as being in the range of 1.5–4 kcal/mol, depending on the calculation methods utilized. Inspired by the results of lone-pair electron- π interaction, in 2002 Deyà and coworkers [3] conducted theoretical calculations at HF/6-31++G** and MP2/6-31++G** levels to demonstrate the energetically favored anion- π interaction based on hexafluorobenzene as the π receptors. By using Molecular Interaction Potential with Polarization (MIPp), they pointed out that the main contributions to anion- π interaction are electrostatic and polarization components. The minima for the complexes between anions and the π -cloud of the perfluoroaromatic derivatives were obtained with stabilization energy ranging from –8 to –27 kcal/mol depending on the charge-negative species applied. In this report, Deyà and coworkers termed the interaction between anion and π receptor as “anion- π interaction.” Almost at the same time, Mascàl [2] and Alkorta [4] independently published their theoretical studies describing anion- π interactions. In Mascàl’s work, they reported a MP2/6-31+G* method for the interaction of 1,3,5-triazine and trifluoro-1,3,5-triazine with anions including fluoride, chloride, and azide. Besides the non-covalent anion- π binding mode in which anion interacts with the centroid of an electron-deficient aromatic ring, minima for both C-H \cdots X $^-$ hydrogen bonding and formation of reactive complexes derived from nucleophilic attack on the triazine ring were also predicted. On the other hand, Alkorta developed DFT (B3LYP/6-31++G**) and MP2 (MP2/6-31++G** and MP2/6-311++G**) ab initio methods to evaluate the interaction of anions with perfluorobenzene compounds. It is very interesting to note that although anion- π interaction predicted by most of the calculations is attributed to the electrostatic and polarization effects, different opinions have also appeared in literature. Kim and coworkers [18], for example, have carried out high-level ab initio calculations and used symmetry-adapted perturbation theory (SAPT) method to investigate the nature of anion- π interactions. Except for electrostatic and induction energies, they suggest that the contribution from dispersion energy is substantial for anion- π interaction. Being different from most of the theoretical studies focusing the typical non-covalent anion- π interaction mode, viz., the interaction of anion with the centroid of electron-deficient aromatics, Hay and his coworkers [19] emphasized varied anion- π interaction motifs. On the basis of MP2/aug-cc-pVDZ calculations of the interactions of F $^-$, Cl $^-$, and Br $^-$ with 1,2,4,5-tetracyanobenzene (TCB), 1,3,5-tricyanobenzene, triazine, and hexafluorobenzene, they proposed three distinct energetically favored complexes as depicted in Fig. 1. Recently, Xu [20] set up a highly accurate extended ONIOM (XO) method based on double-hybrid density functional XYG3/6-311++(d,p) level to understand the anion- π nature in depth. They applied specific systems involving tetraoxacalix[2]arene[2]triazine and four anions including SCN $^-$, NO $_3^-$, BF $_4^-$, and PF $_6^-$. With the optimized structures, contribution and strength of anion- π and other non-covalent interactions were systematically analyzed. This novel theoretical method provides new angle on the study of anion- π interactions.

10.3 Representative Experimental Evidences of Anion- π Interactions

At the early stage after the theoretical predictions on anion- π interactions, many endeavors have been made to exemplify such non-covalent interaction from experiment. Here we gave some representative examples that have single crystal structures to definitely support anion- π interaction. In 2004, Meyer and coworkers prepared copper (II) chloride complexes with hexakis(pyridine-2-yl)-[1,3,5]-triazine-2,4,6-triamine as ligand (Fig. 2a) [21]. In the single crystal structure, the complex contains chloride (Cl^-) and $[\text{CuCl}_4]^{2-}$ as counteranions. The most interesting feature of the complex is chloride ($\text{Cl}8$) resides above one of the triazine rings. The distance between the centroid of the ring and chloride is 3.17 Å, and the angle of $\text{Cl}^- \cdots$ centroid axis to the plane of ring is 87° . The two structural features are highly in line with the theoretical prediction of typical anion- π interaction. In the same year, Reedijk et al. [22] provided a Cu (II) complex structure describing the interaction between pyridine and chloride using a pyridine- and triazine-containing ligand. In this report the encapsulation of one chloride anion by four pyridine rings was demonstrated as a result of possible anion- π interaction between them (Fig. 2b).

Despite the fact that anion- π could be found in many metal coordination complexes, the main argument lies in that it is difficult to distinguish the contribution between anion- π interaction and intrinsic Coulombic interaction. In this context, electron-deficient charge-neutral organic molecules could provide ideal platform to elucidate and probe the contribution of anion- π interactions. However, this is a rather challenging task. Only limited examples demonstrating unambiguously anion- π interactions can be found in literature till now. In 2004, Kochi and coworkers [23] reported their study of the interaction between anions and a series of neutral organic π receptors including tetracyanobenzene (TCB), 1,3,5-trinitrobenzene (TNB), 2,3,5,6-tetracyanopyrazine (TCP), 2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione (p-CA),

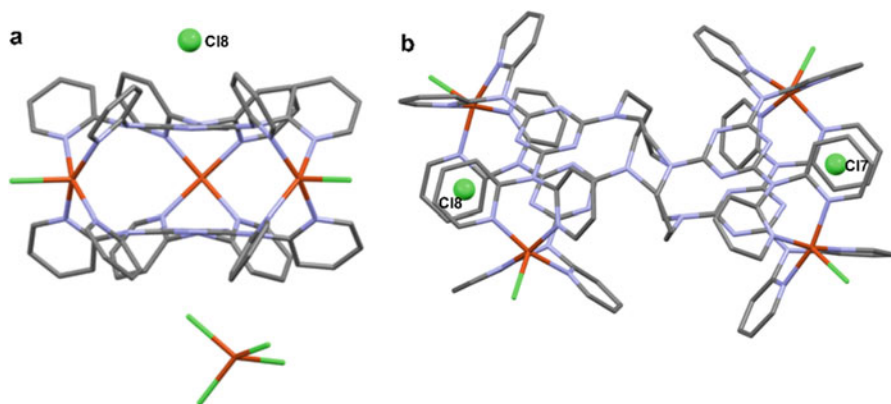


Fig. 2 Crystal structure of anion- π interactions in coordination systems by (a) Meyer and coworkers and (b) Reedijk and coworkers

3,4,5,6-tetrachlorocyclohexa-3,5-diene-1,2-dione (o-CA), and 1,1,2,2-tetracyanoethene (TCNE). From the crystal structure of the complexes formed with halides and TCP (Fig. 3), for example, halides are found to shortly contact with carbon atom of the π receptors, giving $X^- \cdots C$ distances in the range of 2.93–3.49 Å. These structures indicated the formation of weak σ -type rather than typical anion- π interaction. Spectral and thermodynamic study revealed the charge-transfer origin between the donor and acceptor in the complex. Similar binding modes of TCB and Br^- , I^- , respectively, were also demonstrated by Hay and coworkers in 2007 [19]. In the complexes that four TCB molecules contacted each anion, three distinct orientations, i.e., above the arene plane nearest to a carbon bearing a CN group, above the arene plane nearest to a carbon bearing a hydrogen atom, and nearly within the plane of the arene contacting a C-H hydrogen atom, were observed.

Typical non-covalent anion- π interaction was firstly reported by us in 2008 [24]. The study was based on a tetraoxacalix[2]arene[2]triazine molecule **1**, a unique molecule bearing a V-shaped cleft formed with two electron-deficient triazine rings and halides. As unveiled by the X-ray crystallography (Fig. 4), **1** formed ternary complex with one halide anion and a water molecule. The included chloride or bromide located almost over the center of one of the triazine rings, with a vertical distance to triazine plane being 3.218–3.247 Å ($d_{Cl-plane}$) or 3.273–3.348 Å ($d_{Br-plane}$), respectively. The short distance of halide to the triazine centroid indicated convincingly a typical non-covalent anion- π interaction. Concurrently, the water molecule, which was hydrogen bonded to halide, forms $H_2O \cdots \pi$ (lone-pair electron- π interaction). Later in 2013, we [25] demonstrated the generality of anion- π

Fig. 3 Weak σ -type interaction between TCP and chloride demonstrated by Kochi and coworkers

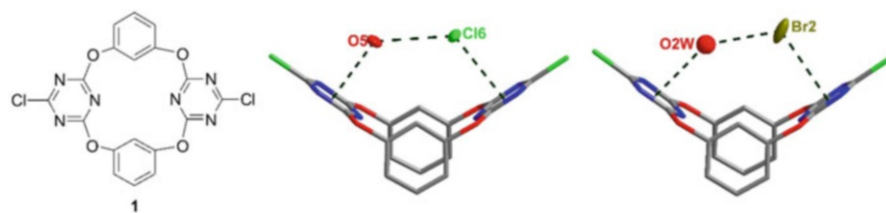
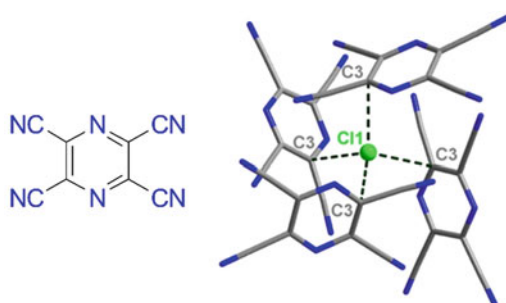


Fig. 4 Complexation of tetraoxacalix[2]arene[2]triazine **1** with Cl^- and Br^- through typical anion- π interactions

interactions with the same host and anions of varied geometry including linear thiocyanate (SCN^-), triangular nitrate (NO_3^-), tetrahedral tetrafluoroborate (BF_4^-), and octahedral hexafluorophosphate (PF_6^-). The complexations as revealed by X-ray crystallography showed clearly that anions despite their various geometries form 1:1 complexes with **1**. Typical anion- π interaction was ubiquitously observed in all complexes; besides, concurrent σ -type interaction was also found depending on the specific geometry of the anion (e.g., in $[\text{1}\cdot\text{NO}_3]^-$ complex) (Fig. 5).

We have also applied a conformationally rigid cage molecule bis(tetraoxalix[2]arene[2]triazine) **2** containing three identical electron-deficient V-shaped clefts to demonstrate various halide- π geometry [26]. In the complex of **2** with chloride (Fig. 6), chloride (Cl_2) was situated above the carbon atom of triazine ring with chloride-carbon distance ($d_{\text{Cl}(2)-\text{C}(2)}$) being 3.342 Å, indicating a weak σ -type interaction ($\text{C}\cdots\text{Cl}^-$). To complex bromide, however, host **2** self-regulated its structure yielding three V-shaped clefts of different sizes; each cavity provided different bromide- π interactions. In the smallest cleft, bromide (Br_2) anion formed close contact with one of the triazine rings forming typical anion- π interaction ($d_{\text{Br}2-\text{triazine}} = 3.429$ Å). In the largest cleft, however, a bromide and water were included within the cavity through concurrent anion- π ($d_{\text{Br}1-\text{triazine}} = 3.516$ Å) and $\text{lpe}-\pi$ ($d_{\text{O}4-\text{triazine}} = 2.892$ Å) interactions.

In 2013, Stoddart and coworkers [27] reported the anion- π interaction between a NDI-containing triangular cage molecule **3** and linear I_3^- anion. The solid-state complex structure revealed I_3^- anion almost completely fills up the tube-shaped cavity of the triangular molecular prism (Fig. 7).

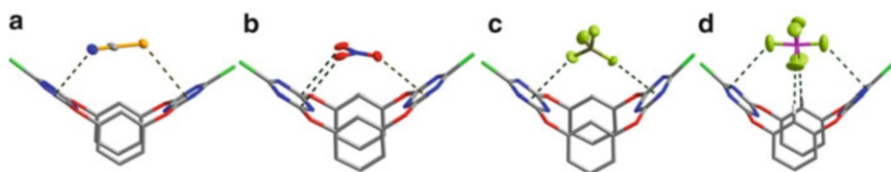


Fig. 5 Anion- π complexes formed with tetraoxalix[2]arene[2]triazine **1** and (a) SCN^- , (b) NO_3^- , (c) BF_4^- , and (d) PF_6^-

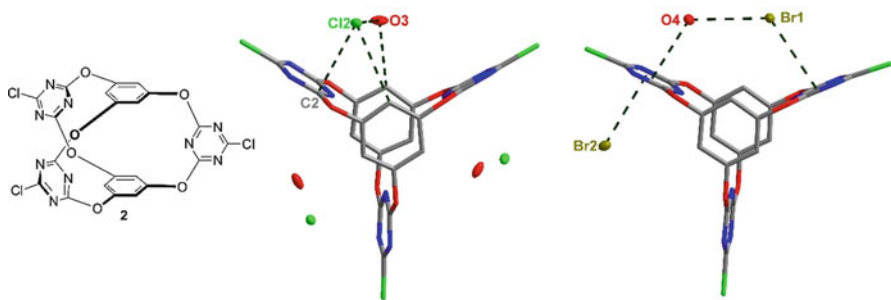


Fig. 6 Different types of anion- π interaction formed with **2** and chloride and bromide

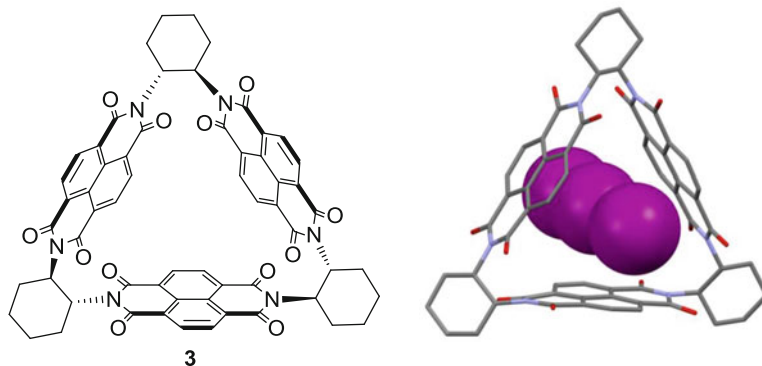


Fig. 7 Anion- π interaction between a NDI-containing triangular cage and I_3^- anion by Stoddart and coworkers

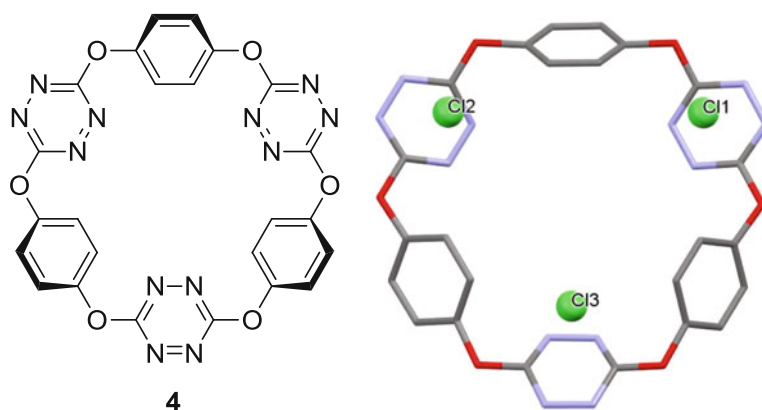


Fig. 8 Anion- π interactions between corona[3]arene[3]tetrazine **4** and chlorides by Wang and coworkers

Tetrazine as an amusing π -receptor has been incorporated into a novel type of macrocyclic host molecules named coronarenes by Wang and coworkers [28]. The existence of tetrazine component in the macrocyclic backbone rendered the molecules electron-deficient property. As a representative example, O_6 -corona[3]arene[3]tetrazine formed a 1:3 complex with Et_4NCl in solid state. Each of the three chlorides in the complex located above each tetrazine centroid at a distance of 3.06–3.20 Å, forming typical anion- π interactions (Fig. 8).

It is also worth noting that anion- π interactions were detected as modulations of stronger non-covalent interactions such as hydrogen bonding [29, 30] and ion-dipole interaction [31]. Albrecht and coworkers reported the binding of pentafluorobenzamide toward bromide through cooperative H-bonding and anion- π interaction [29]. Single crystal structure demonstrated that bromide located above the plane of pentafluorobenzene ring and concurrently formed hydrogen bonding

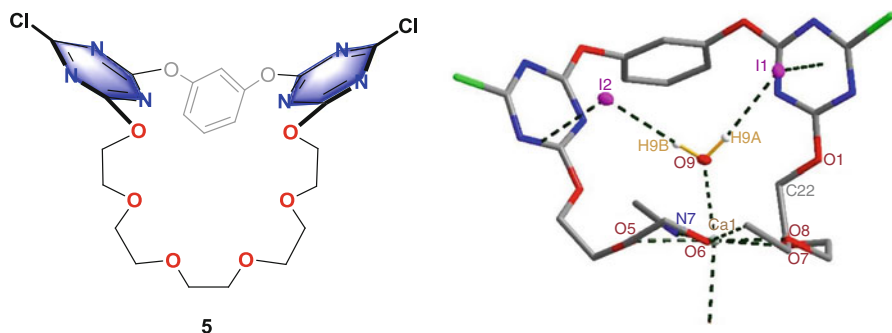


Fig. 9 Crystal structure of the solvent-separated ion-pair complex between **5** and CaI_2

with amide. On the other hand, Ballester and coworkers [30] used “two-wall” aryl-extended calix[4]pyrrole as model system and studied the thermodynamic characterization of halide- π interaction in solution. The solid-state structures of the inclusion complexes revealed that chloride was not located directly perpendicular to the centroid of the phenyl rings but somewhat offset.

Very recently, with a rational designed tritopic ion-pair receptor **5** [31], we demonstrated an unusual solvent-separated ion-pair complex with CaI_2 . Single crystal structure revealed that the two iodides, respectively, were stabilized by each triazine ring through anion- π interactions ($d_{\text{I1-plane}} = 3.621 \text{ \AA}$, $d_{\text{I2-plane}} = 3.649 \text{ \AA}$), while the calcium ion (Ca1) was bound by four oxygen sites of the pentaethylene glycol chain, two axial water molecules, and one acetonitrile molecule. The two iodides and calcium ion resided in a triangular array, with the water molecule (O9) nearly occupying the center position and separating the iodide-calcium ion pairs through two H-bonds. Such array is distinctively different from the regular octahedral lattice of CaI_2 , demonstrating the stabilization contribution from both the cation and anion binding sites within the receptor (Fig. 9). In another work, we reported a significant conformational control of oxacalix[3]arene[3]triazine macrocycle with anion- π interactions [32]. In solid state, the macrocycle showed relatively flexible conformation, giving a tighten-waist 1,3,5-alternate conformation. After complexation with halides through anion- π interactions, the macrocyclic backbone underwent dramatical conformation changes. For complexation with chloride, a pyramidal conformation was resulted, whereas a C_3 -symmetric 1,3,5-alternate conformation was observed for complex with bromide.

10.4 Anion-Templated Self-Assembly

In most anion- π -related coordination complexes, anions act mainly as counterions to compensate the positive charge; anion- π therefore slightly affects the assembly structure. Remarkably, Dunbar and coworkers reported comprehensive investigation of anion-templated self-assemblies, where anion- π plays important

roles in controlling the assembly structures [33–36]. In 2005 they performed a reaction of first-row transition metal ions with bis-bipyridine ligand (bptz) in the presence of specific anions [33]. Cyclic structures were obtained with Ni(II), Zn(II), and Fe(II) as revealed by X-ray crystallography. The decisive roles of anions in the formation of a particular cyclic structure were carefully discussed. Interestingly, among the different anions encapsulated inside the metallacages, small anions such as BF_4^- and ClO_4^- led to molecular squares, whereas the larger anion SbF_6^- favored pentagon structure (Fig. 10). Alternatively, the reaction of $[\text{Ni}(\text{CH}_3\text{CN})_6]$ $[\text{NO}_3]_2$ with bptz in a 1:1 ratio produced probably a triangular structure as supported by MS and IR. It was found that treating the pentagon sample with an excess of BF_4^- or ClO_4^- anion led to the complete conversion of pentagon to square. The reverse transformation, however, needs forcing conditions such as a large excess of SbF_6^- , reflux, and long reaction time, and then a partial transformation of the square to the pentagon took place. Careful examination of the relevant structural parameters suggested by the authors that cyclic structures may be stabilized by anion- π interactions as judged from the short distances between centroids of tetrazine rings with the O/F atoms of the encapsulated anions. A more comprehensive investigation of anion- π interactions was later performed by the same group [34]. They combined crystallographic and computational methods that systematically studied the roles of anion- π interactions in Ag(I) complexes with tetrazine-containing bptz or pyridazine-containing bppn ligands, respectively. The theoretical optimizations revealed the central ring of bptz (tetrazine) shows higher electropositive character than that of bppn (pyridazine). They found the higher π -acidity of tetrazine renders bptz amenable to anion- π rather than π - π interactions. In all the Ag(I)-bptz complexes, anion- π interactions were generally observed. The different anion- π details corresponding to

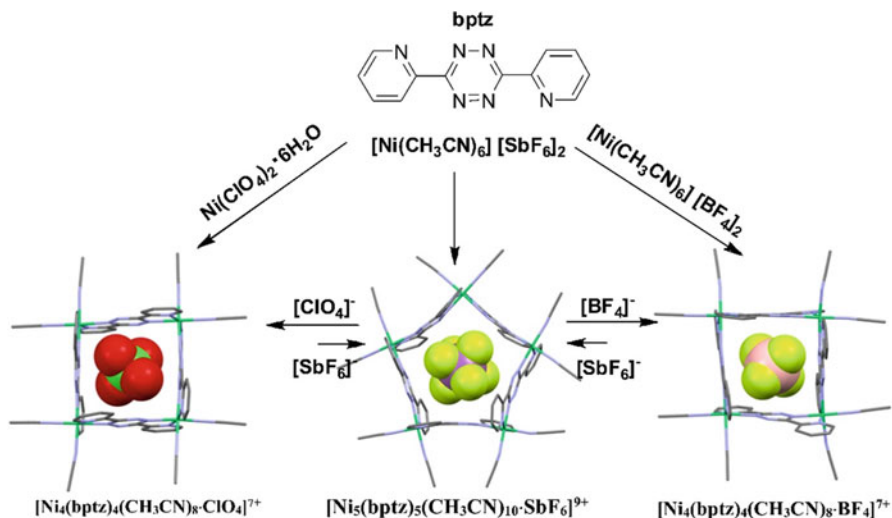


Fig. 10 Structure of anion-templated complexes and their scheme of interconversion by Dunbar and coworkers

different anions determined the resulting assemblies as polymer, planar dinuclear, or propeller-type dinuclear structures. Whereas the Ag(I)-bppn complexes gave rise to grid-type structures regardless of the anion, which is attributed to the electron-rich π -ligand favors the maximized π - π stacking at the expense of anion- π interactions. Taking the Fe(II) metallacycles as examples, Dunbar and coworkers [35, 36] applied ^{19}F NMR spectroscopy to provide evidence that anion- π interactions are the main driving force in the templating process leading to particular structures in solution. Whereas random Fe(II)/bytz oligomers were formed in the presence of non-templating anions such as CF_3SO_3^- , closed polygons were favored in the presence of templating anions including BF_4^- , AsF_6^- , and SbF_6^- . At elevated temperature, the considerable broadening ^{19}F NMR resonance indicated rapid exchange of the encapsulated anions with free species, while lowering the temperature led to broadening of ^{19}F NMR resonance of polygons, and a second distinct ^{19}F NMR resonance corroborating the presence of encapsulated anions occurred. From the low activation energy determined, the authors concluded that anions acted as templates rather than merely diffusing into preformed cages.

In another report by Choi et al. [37], they set up mechanochemical reactions of 3,6-dimethoxy-s-tetrazine (dmoz) with AgCF_3SO_3 and AgClO_4 . Different structures such as 1D linear polymer ($[\text{Ag}(\text{dmoz})(\text{CF}_3\text{SO}_3)]_n$) or 2D grid polymer ($[\text{Ag}(\text{dmoz})_2(\text{ClO}_4)]_n$) were obtained depending on the specific anions applied. Intermolecular anion- π interactions between tetrazine ring and CF_3SO_3^- , for example, led to the tightening of 1D linear chains, whereas ClO_4^- was surrounded with four tetrazine rings which provided the 2D structure.

10.5 Self-Assembly with Anion as Primary Building Blocks

As the main challenge in anion-templated self-assemblies (*vide supra*) is that it is difficult to distinguish the contribution of anion- π and coordination interactions, using charge-neutral π receptor as one building component to probe anion- π -directed assembly is therefore particularly intriguing. However, due to the flexible directionality of anion- π non-covalent bond, this task is very challenging, and the early examples that appeared in literature were mainly observed in crystal structures. The rational design of anion- π -controlled self-assembly based on charge-neutral building blocks emerged until very recently.

10.5.1 Self-Assembly with Electron-Deficient Arenes

In 2008, Kochi et al. [38] examined the behavior of a series of planar π -acids toward various types of polyatomic anions by means of crystallography. They demonstrated from about 20 crystal structures that similar repeating anion/ π -acid arrangement consisting of a vertical one-dimensional (1D) stack of π -acid alternatively interspersed with the π -bonded anions (Fig. 11). Anions interacted with the carbon atom of π -acid molecule forming the so-called σ -type interaction. The location of anions

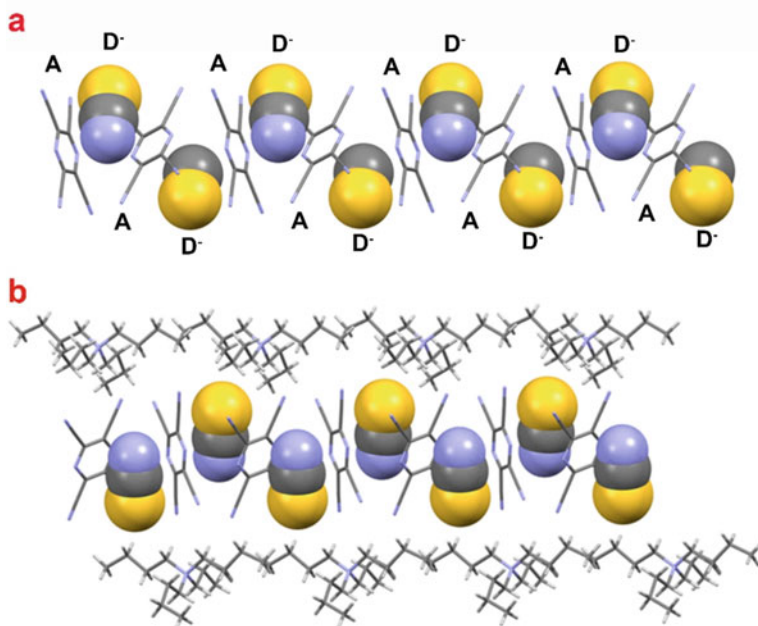


Fig. 11 Linear 1D molecule “wire” formed with TCP and tetrabutylammonium thiocyanate by Kochi and coworkers, (a) anion/ π -acid chain without TBA⁺, and (b) with the protecting sheath of TBA⁺

over the π -acid showed subtly different details depending on the specific geometry of anions. Consequently, the atom-to-atom distances for the σ -type interactions were in the range of 2.79–3.45 for different anionic species. Every π -acid molecule is precisely arrayed with specific dihedral angles (plane to plane). A 3:2 (anion to π -acid) ratio was regarded as the repeated unit to lead to indefinite 1D molecular “wire” ($\cdots D^- A D^- A D^- A \cdots$). Another character of the self-assembly is π -acid/anion wire is surrounded by the sheath of counteranions (e.g., TBA⁺) and then was isolated from its neighboring 1D wire. By means of UV-vis spectroscopy, the authors investigated the charge transfer (CT) between π -acid molecules and anions, and they believed CT plays critical roles on the linear 1D molecular arrays.

In 2010, Dunbar and coworkers [12] reported 1D vertical chain self-assembly with a strong π -acidic arene hexaazatriphenylene-hexacarbonitrile (HAT(CN)₆) and anionic halides as building units. The cocrystallization of HAT(CN)₆ with [n-Bu₄N]⁺X⁻ (X = I⁻, Br⁻) afforded isostructural analogs $\{([n-Bu_4N][X])_3[HAT(CN)_6]_2\} \cdot 3 C_6H_6$. From these structures, infinite chains $\{[HAT(CN)_6]_2X_3\}^{3-} \cdots X^- \cdots \{[HAT(CN)_6]_2X_3\}^{3-} \cdots X^- \cdots \{[HAT(CN)_6]_2X_3\}^{3-}$ consisting of layers ABCD as the repeated units were formed. Two types of anion-HAT(CN)₆ interactions were revealed from the ABCD entity. One X⁻ (X = I⁻, Br⁻) showed short contact with the centroid of HAT(CN)₆ (layer C and D), giving anion-centroid distances shorter than the sum of van der Waals radius, which is in line with

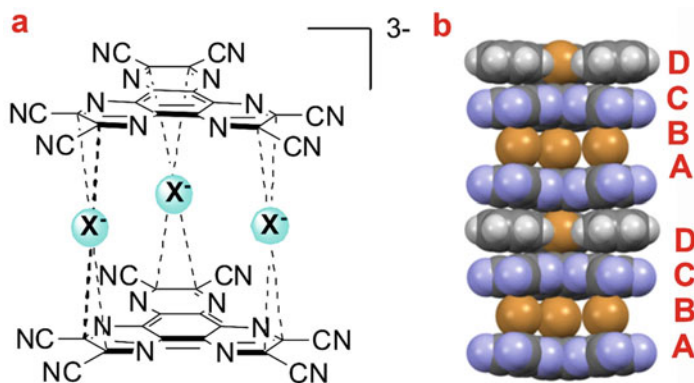


Fig. 12 1D vertical chain self-assembly between HAT(CN)₆ and halide by Dunbar and coworkers

typical anion- π interaction. Furthermore, each of the three equivalent X^- is located over the periphery of HAT(CN)₆ (layer A–C), forming σ -type interactions in an η_2, η_3 fashion (Fig. 12).

10.5.2 Self-Assembly with Macrocyclic Molecules

To address the challenge on rationally designing self-assembly motifs directed by anion- π interaction, we envisioned that tetraoxacalix[2]arene[2]triazine backbone could serve as an ideal building unit. The 1,3-alternate macrocyclic backbone bears a V-shaped cavity formed with two convergent electron-deficient triazines. We have shown that the V-shaped cavity is able to include a variety of anions through anion- π interactions [24, 25]. The bridging oxygen atoms endow the cavity with fine-tunable properties and allow the best fit of a given anion, thus leading to a good control on the interaction directionality.

In 2010 [26], we reported the two-dimensional self-assembly with bis(tetraoxacalix[2]arene[2]triazine) **2** and halide anions X^- ($X = Cl^-, Br^-$) interacting entities. Slow evaporation of the solvent from mixture of **2** and tetraethylammonium halides at room temperature afforded complexes of $[2-(Et_4NCl)_3-(H_2O)_3]$ and $[2-(Et_4NBr)_2-H_2O]$, respectively. Different self-assembly structures were observed depending on the type of halides involved. In the case of $[2-(Et_4NCl)_3-(H_2O)_3]$ complex, the organic building block remained as D_{3h} symmetry and therefore gives three identical V-shaped cavities. Each V-shaped cleft accommodated one chloride anion through weak σ -type interaction (vide supra) and one H₂O molecule through lone-pair electron- π interaction, and the two included species were hydrogen bonded to each other. Then the hydrogen-bonded chloride-water pair in each V-shaped cleft interacted with other pair of chloride-water that belongs to other complex entity, forming a hydrogen bonding network. Six cage-anion-water entities cyclized into a repeat unit, affording to a two-dimensional honeycomb-like self-assembly (Fig. 13a). In the case of complex $[2-(Et_4NBr)_2-H_2O]$, the demand

for versatile bromide- π interactions led to a significant conformation change of the cage molecule, producing three V-shaped clefts of different sizes (*vide supra*). Multiple non-covalent interactions including bromide- π , lpe- π , and hydrogen bond led to capsule-like structure as repeat units, affording infinite two-dimensional self-assembly (Fig. 13b).

To further take advantage of the chloride- π interaction to induce self-assembly, we designed phenoxy-substituted tetraoxacalix[2]arene[2]triazine building block **6** and investigated the self-assembly with chloride [39]. In the absence of chloride, the building block itself showed unique self-assembly. For example, one triazine nitrogen of one molecule **6** formed lone-pair electron- π interaction with the triazine of another molecule. In addition, weak intermolecular hydrogen bonds between hydrogen bond acceptor such as triazine nitrogen, bridging oxygen, and aryl hydrogens were also observed. Directed by the multiple weak non-covalent interactions, **6** formed a cyclic hexamer structure in solid state. In the presence of chloride, the cyclic hexamer self-assembly of building block **6** was disrupted and transformed into a rectangular cage structure. The driving forces for this transformation were revealed. Chloride- π interaction ($d_{\text{chloride-plane}} = 3.238 \text{ \AA}$), water- π (lone-pair electron- π), and chloride-water hydrogen bond facilitated the formation of ternary complex. Two ternary complexes provided a rectangular cage structure with the help of hydrogen bond network between chloride and water and π - π stacking between two face-to-face arrayed benzene rings (Fig. 14). In our another work, we designed organic building block by introducing hydroxyl substituents on the larger rim of tetraoxacalix[2]arene[2]triazine **7** and studied its self-assembly with anions [40]. The hydroxyl group served as lone-pair electrons and hydrogen bond donor instead of the aforementioned water molecule to form host-halide-hydroxyl ternary complex. As hydroxyl is covalently attached on the building block, such ternary complex led to an infinite linear self-assembly (Fig. 15).

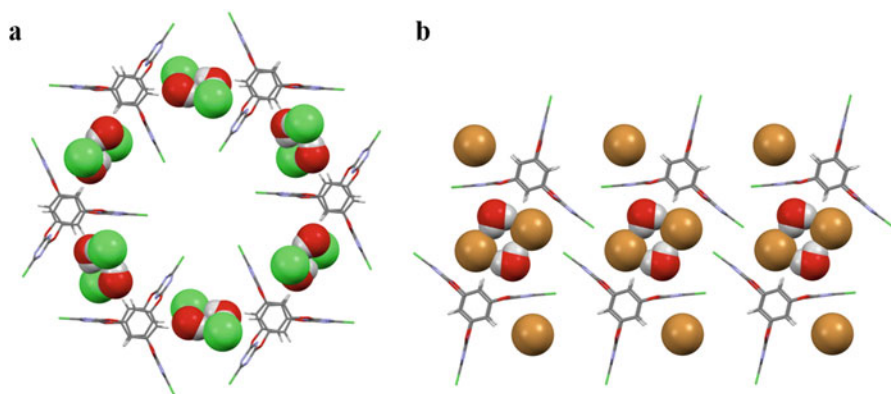


Fig. 13 (a) Honeycomb-like self-assembly formed with cage molecule **2** and chloride and (b) two-dimensional self-assembly formed with cage molecule **2** and bromide

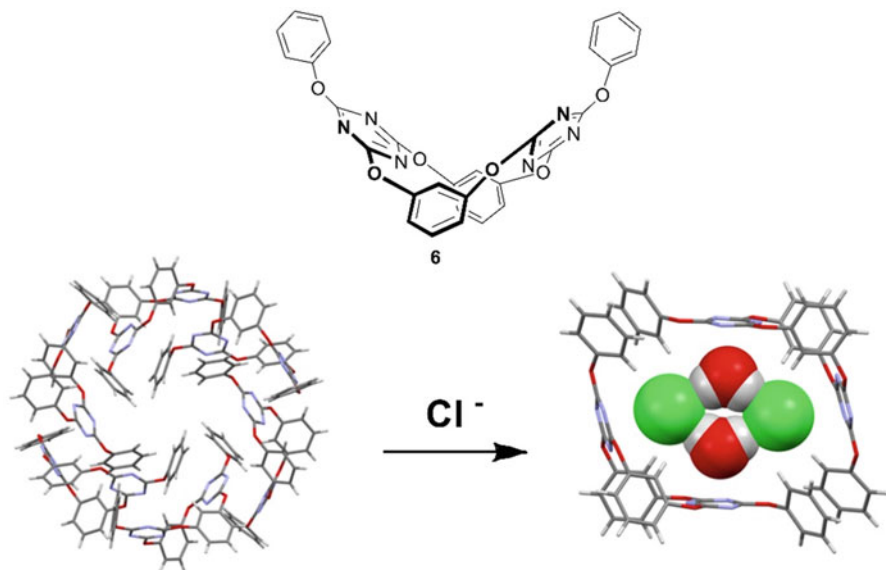


Fig. 14 Chloride-induced self-assembly transformation from cyclic hexamer to rectangular cage structure through anion- π non-covalent interactions

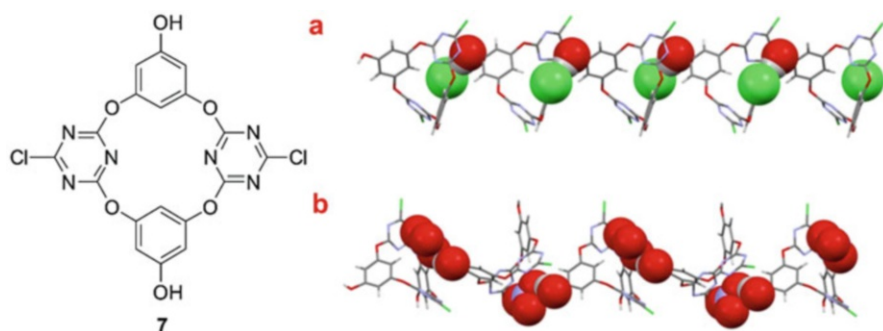


Fig. 15 Infinite self-assembly formed with hydroxyl-substituted tetraoxacalix[2]arene[2]triazine **7** and anions, (a) chloride, (b) nitrate

In 2017, we designed [41] a series of tetraoxacalix[2]arene[2]triazines **8** bearing different anionic heads such as carboxylate, sulfonate, sulfate, and phosphate. These molecules served as dual building units with the V-shaped electron-deficient cavity as anion binding site, whereas the anionic head as the “guest.” With this rational design, anion- π self-assembly was firstly investigated in solution. It is worth noting that when anion- π interaction between anion and triazine rings occurs, the low-rim hydrogen atom (e.g., H_1 , H_2 , toward the cavity) can be forced to participate the anion binding via weak hydrogen bonding, which enables the monitoring of self-assembly behavior with NMR technique.

From the recorded ^1H NMR spectra of **8** at variable concentrations, H_1 and H_2 did downfield shift gradually upon concentration increase, while other proton signals almost remained intact. This suggested intermolecular interaction would occur with the anionic head being included within the V-shaped cavity of another molecule through weak hydrogen bonding along with the dominant anion- π interaction. The assembly behavior was further confirmed by variable temperature (VT) ^1H NMR where upfield shift of H_1 and H_2 was observed from 25 $^\circ\text{C}$ to 75 $^\circ\text{C}$, in line with disfavored assembly (disassembly) at elevated temperature (Fig. 16). The supramolecular aggregation was further investigated by diffusion-ordered NMR spectroscopy (DOSY) and dynamic light scattering (DLS). As expected, in all the cases for the dual building blocks, diffusion coefficient gradually decreased upon concentration increase. On the other hand, the hydrodynamic radius of aggregates as determined by DLS gradually increased upon increasing sample concentration. Both techniques indicated larger and larger assembly formation during the self-assembling course. The aggregation was further evidenced by electrospray ionization mass spectrometry (ESI-MS), from which monomeric, dimeric, and trimeric peaks were observed. In solid state, single crystal structures gave detailed insight of the intermolecular self-assemblies. For the three compounds bearing carboxylate, sulfonate, and sulfate, the anionic head was included within the V-shaped cavity of another adjacent molecule through anion- π interaction along with weak hydrogen bonding. As such, 1D chain-like assembly was formed with the shape of the chain

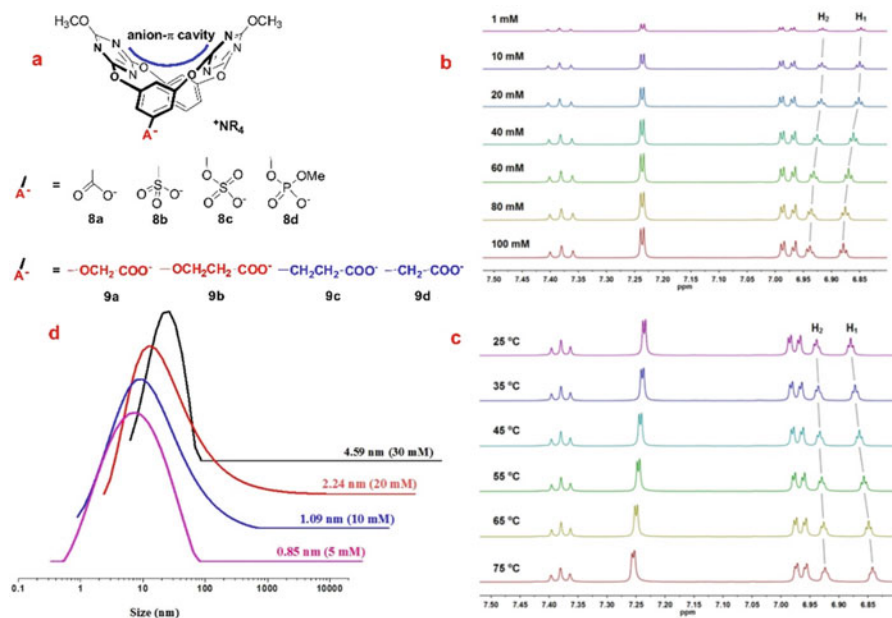
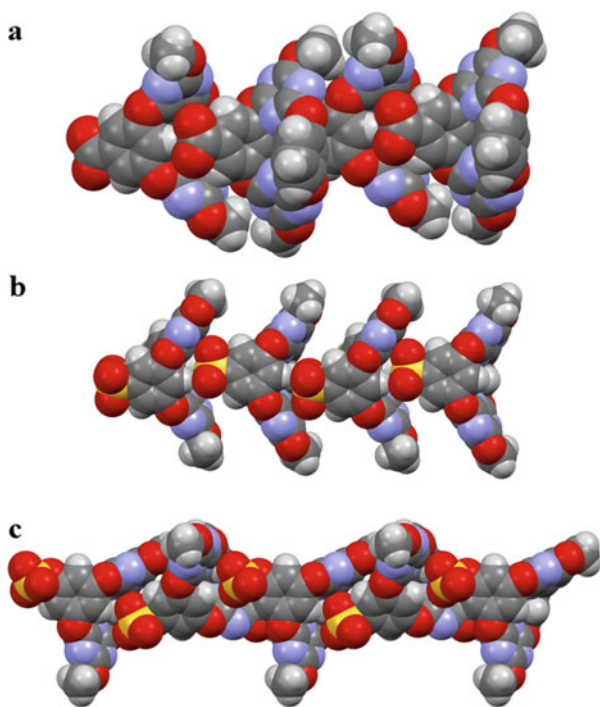


Fig. 16 Dual building blocks **8** (a), self-assembly of **8b** in solution studied by ^1H NMR spectra of variable concentration (b), variable temperature (VT) (c), and DLS results (d)

being affected by the specific anionic head involved (Fig. 17). When flexible linkers were introduced in between the benzene ring of the macrocycle and carboxylate head (**9**), the ability to form self-assembly was diminished due to the increased flexibility of anionic head and was dependent on the linkers applied. The existence of oxygen leads to linker being more flexible, which is unfavorable to the intermolecular complexation [42].

Very recently, self-assembly between bisoxacalix[2]arene[2]triazines **10–13** (Fig. 18), in which two macrocyclic motifs are linked at their larger rim, and naphthalene-1,5-disulfonate dianion was investigated. The anion- π -driven self-assembling processes were systematically studied by means of ^1H NMR spectra and DLS in solution, combination of SEM, TEM, and AFM on surface [43]. While both concentration-variable ^1H NMR and VT ^1H NMR of an equimolar host-guest mixture supported progressive formation and disassembly of the oligomeric species, DLS measurements gave evidence of larger species formation. In DLS, peaks corresponding to the oligomeric species at small size and very large aggregates (average size of 735 nm) were observed. Remarkably, after extensive supersonic of the concentrated solutions at different host-guest ratios ($[\text{host}] = 20 \text{ mM}$), significant Tyndall effect was observed under the irradiation of laser beam, supporting the formation of colloidal aggregates as observed by DLS. The morphology of the host-guest self-assembly was revealed by SEM, TEM, and AFM techniques.

Fig. 17 1D chain-like structures of dual building blocks (a) **8a**, (b) **8b**, and (c) **8c** in solid state



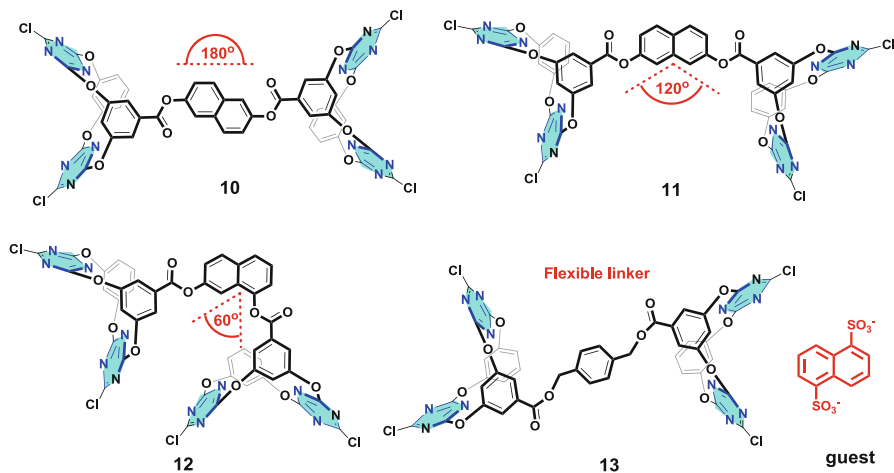


Fig. 18 Bisoxacalix[2]arene[2]triazines as dual building units of anion- π self-assembly

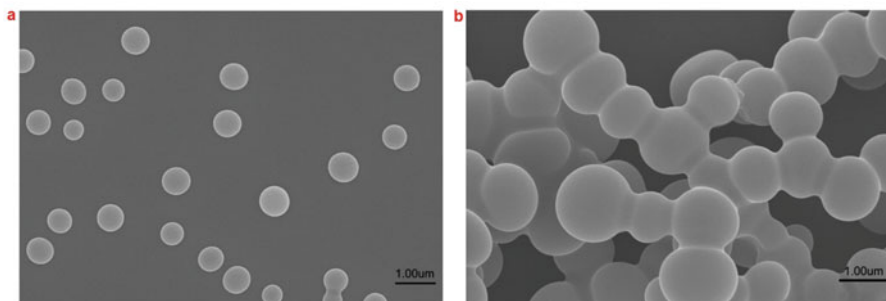


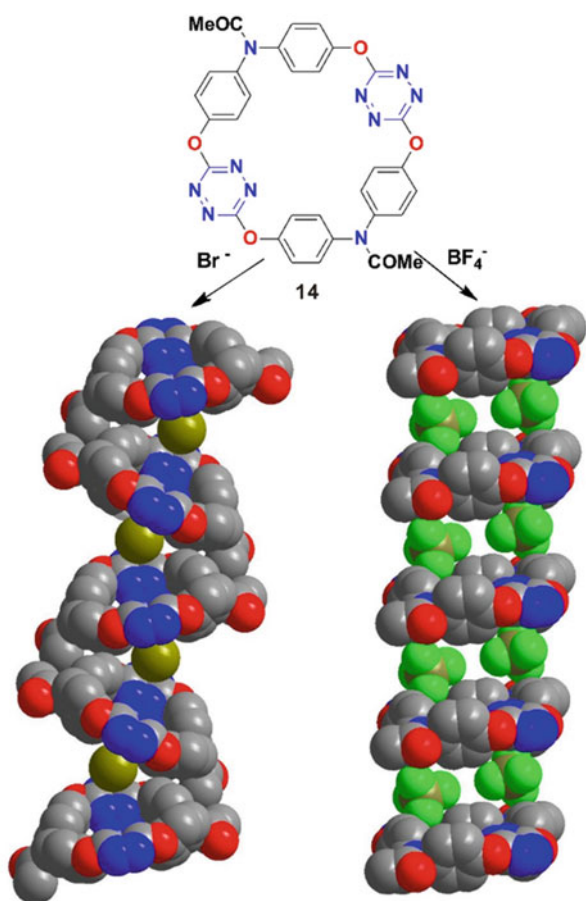
Fig. 19 Self-assembly of **11** in the absence (a) and presence (b) of naphthalene-1,5-disulfonate

Surprisingly, coherent particles were formed in the presence of an excess of **11–13**, as confirmed by SEM, TEM, and AFM images (Fig. 19). To probe the contribution of anion- π interaction, energy dispersion spectroscopy (SEM-EDS) analysis was carried out, and peak for element S from naphthalene-1,5-disulfonate was also clearly observed. Particularly, the intensity analysis suggested that the S component was mainly concentrated in the joint parts of the coherent particles. On the other hand, experiments with naphthalene-1,5-disulfonic acid and naphthalene-1-sulfonate as control compounds did not give the as-mentioned coherent particles, demonstrating the essential role of anion- π interaction in self-assembly formation.

Diverse self-assembling structures afforded with interaction between corona[4]arene[2]tetrazine **14** and anions of different geometries were demonstrated by Wang and coworkers [44]. In solid state, **14** formed complexes with various anions

including spherical Cl^- , Br^- and I^- , linear SCN^- , planar triangular NO_3^- , tetrahedral BF_4^- and ClO_4^- , and organic anion naphthalene-1,5-disulfonate. All complexes involved typical anion- π interactions between anion and tetrazine moiety with only the exception of complexation with nitrate in which anion interacted with tetrazine through σ -type interactions. Most anions were sandwiched by two tetrazine rings from two macrocycles. Depending on the nature of anions, and due to the effect of different non-covalent bonds between anions and coronarenes, varied self-assemblies were generated. For example, Cl^- , Br^- , I^- , SCN^- , and ClO_4^- induced the host-guest to one-dimensional chain-like structure, while the presence of BF_4^- afforded an interesting ladderlike self-assembly. Different to the organic anions, the organic anion naphthalene-1,5-disulfonate appeared to be encapsulated by two coronarene molecules, each complexed capsule assembled into a linear structure through DMSO solvent which associated with other tetrazine ring of coronarene via a lone-pair electron- π interaction (Fig. 20).

Fig. 20 Self-assembly of **14** with bromide (left) and tetrafluoroborate (right) by Wang and coworkers



10.6 Self-Assembly with Anions as Secondary Building Blocks

Taking tetraoxacalix[2]arene[2]triazine as a functionalization platform, we designed a series of amphiphilic molecules by introducing long alkyl chains on the larger rims [45]. These amphiphilic molecules self-assembled into stable vesicles in a mixture of THF and water, with the surface of the vesicles engineered by electron-deficient cavities. When anions including NO_3^- , F^- , Cl^- , Br^- , BF_4^- , SCN^- , and ClO_4^- were allowed to interact with the vesicles and monitored with DLS, the size of self-assembled vesicles were selectively influenced, giving a selectivity of $\text{F}^- < \text{ClO}_4^- < \text{SCN}^- < \text{BF}_4^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^-$. As the effect of anions on vesicles is almost in agreement with the order of binding constants at molecular level, it indicates that anion- π interaction most probably competed over other possible weak interactions and accounts for this interesting selectivity. Upon the affinity of vesicular surface to anions, the change of the surface zeta (ζ) potential of the vesicles might contribute to the enlargement of vesicles. Later we designed macrocyclic amphiphiles bearing different hydrophilic substituent groups on the larger rim of the triazine rings, in order to explore the self-assemblies of amphiphilic molecules and to probe the responses of vesicles toward anions in water [46]. The nature of substituents showed significant effect on the self-assembly, only substituents with proper hydrophilicity and length could form vesicles. Vesicular surface-anion study confirmed the function of anion- π interaction and enhanced regulation as a result of cooperative anion- π and hydrogen bonding. Very recently, we further modified the macrocyclic amphiphiles by introducing L-prolinol on triazines [47]. The resulting vesicles formed with this amphiphiles are decorated by chiral cavities on the surface and show selective response to chiral anions including (2*S*, 3*S*)-2,3-dihydroxysuccinate (D-tartrate), *S*-mandelate, and *S*-(+)-camphorsulfonate against their respective enantiomers. DFT calculations revealed that the enantioselectivity stemmed from cooperative anion- π interactions and hydrogen bonding between the chiral electron-deficient cavity and the organic anions.

In 2015, we reported an example of anion- π -controlled self-assembly and disassembly [48]. The idea was established on the interaction between tetraoxacalix[2]arene[2]triazine as host molecule and anionic surfactants including sodium dodecyl sulfate (SDS), sodium laurate (SLA), and sodium methyl dodecylphosphonate (SDP) as the guest species. 1:1 mixture of the host-guest solution was quickly injected in water to afford an aqueous solution with final concentration being 6×10^{-4} M. After vortexing for 1 min, the solution produced an opalescent colloidal solution, indicating the formation of self-assembled aggregates. Very low critical aggregation concentrations (CAC) in the range of $5.0\text{--}7.5 \times 10^{-6}$ M were obtained. The vesicular morphology of the aggregates was revealed with SEM, TEM, and XRD techniques. To get more insights on the formation of vesicles, SEM-EDS analysis was set up to reveal the building units of the vesicles. Element peaks corresponding to host and guest were observed, indicating both components contributed to the formation of the vesicles. The anion- π interaction between host and guest was supported by means of HRMS, single crystal structure, and DFT calculation. In other words, host and anionic surfactant formed supramolecular amphiphilic

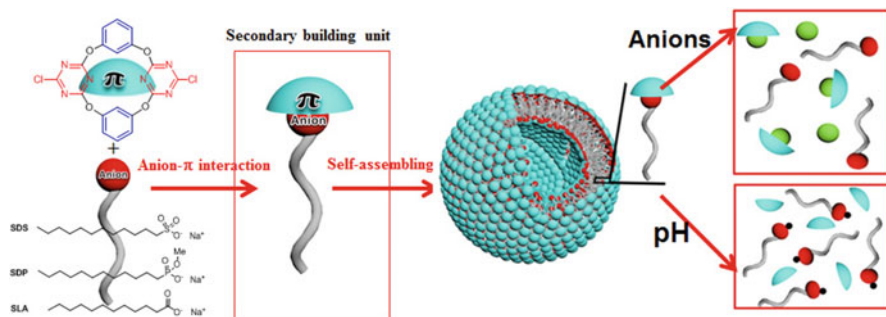


Fig. 21 Anion- π -controlled self-assembly and disassembly

complexes through anion- π interactions. Such complex as secondary building blocks self-assembled into vesicles with the help of cooperative hydrophobic effect of the long alkyl chains. The controlled disassembly of the vesicles under different conditions was revealed. For example, the presence of other competing anions showing stronger interaction with host molecule such as NO_3^- , Br^- , or Cl^- would disrupt the anion- π binding and lead to disassembly of the vesicles to irregular morphologies. Alternatively, the controllable disassembly of the vesicles under decreased pH values was realized by a drug release experiment. A drug doxorubicin was encapsulated into the vesicles, then the vesicles were allowed to various extravascular pH values, and the fluorescent intensity of the encapsulated DOX was monitored. The increased fluorescent intensity with the decrease of pH values indicated the release of DOX, as the protonation of the anionic head of surfactant could weaken the anion- π interaction between host and guest and thus led to the concomitant disassembly of the vesicles (Fig. 21).

In 2017, Tang et al. reported an anion- π^+ -assisted aggregation-induced emission (AIE) system [49]. They constructed AIE-active building blocks of 1,2,3,4-tetra-phenyloxazolium (TPO-P) and 2,3,5-triphenyloxazolium (TriPO-PN) with inherent positive charge. Strong emission of TPO-P and TriPO-PN in the solid state was observed, which was attributed to anion- π^+ interactions that prevent the formation of π - π stacking between two building blocks. In contrast, their charge-neutral analogue did not show AIE effect as a result of aggregation-caused quenching (ACQ).

10.7 Conclusions

As a new type of recognized non-covalent interactions, anion- π interactions as driving force in self-assembly is still in its infancy in comparison with the energetically compatible non-covalent interactions such as hydrogen and halogen bond. The flexible directionality in anion- π interaction is probably the main obstacle. However, the representative findings in this field highlighted herein the fact that anion- π interaction can be important driving force in self-assembly. On one hand, in metal coordination systems, anion- π as additive interaction was responsible for template

effect to afford specific metallacycles. More significantly, anion- π interactions showed ability to drive charge-neutral building blocks and anions into various self-assemblies. With rational designed organic building blocks, the strength and directionality of anion- π interactions could be enhanced; this and along with the intriguing reversibility and easy regulation endow it a promising driving force in rational designed and functional self-assembly.

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